

The Joule-Thomson Coefficient and the Effect of Pressure on the Thermal Properties of Hydrocarbons

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Thermal Properties of Hydrocarbons under Pressure. II

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IN THIS paper the effect of pressure on the isothermal change in enthalpy (H or "heat content") for n -pentane vapor is calculated, using the equation of state suggested by Young, and is found to agree with the experimental data previously reported (5). The effect of pressure on the enthalpy of benzene vapor has been experimentally determined and used in the construction of an enthalpy-pressure-temperature chart. The values for benzene are found to be similar to those for pentane when compared on the basis of the isothermal decrease in enthalpy in B. t. u. per ° R. per pound mole at the same reduced temperature and over the same increment in reduced pressure.

Calculated Enthalpy of Pentane Vapor

In view of the importance and the recent experimental determinations (3, 5, 8) of the enthalpy of hydrocarbon vapors, the following computation based upon rigorous thermodynamic equations and the equation of state for n -pentane developed by Young (10) was made for comparative purposes.

The equation of state,

$$P = \frac{RT}{V} + \left(1 + \frac{e}{V + k - gV^{-2}}\right) - \frac{A}{V(V + k)} \quad (1)$$

in which the constants have the following values,

Constant	Metric Units	Engineering Units
R	863.56	0.1486
e	7.473	0.1197
A	5,420,800.0	26.895
k	3.135	0.0502
g	6.695	0.0000275

was differentiated analytically for the value of $(\delta V/\delta T)_P$ which value was substituted in the following thermodynamic relationship,

$$\left(\frac{\delta H}{\delta P}\right)_T = V - T \left(\frac{\delta V}{\delta T}\right)_P \quad (2)$$

which may be demonstrated:

$$\begin{aligned} dH &= dU + VdP + PdV \\ dU &= TdS - PdV \\ dH &= TdS + VdP \\ \left(\frac{\delta H}{\delta P}\right)_T &= T \left(\frac{\delta S}{\delta P}\right)_T + V \\ dF &= VdP - SdT \end{aligned} \quad \begin{aligned} \left(\frac{\delta^2 F}{\delta T \delta P}\right) &= - \left(\frac{\delta S}{\delta P}\right)_T \\ \left(\frac{\delta^2 F}{\delta P \delta T}\right) &= \left(\frac{\delta V}{\delta T}\right)_P \\ \left(\frac{\delta H}{\delta P}\right)_T &= -T \left(\frac{\delta V}{\delta T}\right)_P + V \end{aligned}$$

The values for $(\delta H/\delta T)_P$ were calculated for three temperatures, 284°, 500°, and 536° F. with pressures up to 1000 pounds per square inch. These curves were then integrated graphically, giving H as a function of P at constant temperature to which must be added the value for H at the initial or atmospheric pressure as a constant of integration.

Similar determinations were made by an entirely graphical method based on the isotherms determined by Young (10) by transforming the thermodynamic equation into the form

$$\left(\frac{\delta H}{\delta P}\right)_T = V - \left(\frac{\delta V}{\delta \ln T}\right)_P \quad (3)$$

and obtaining the values for $(\delta V/\delta \ln T)$, subtracting them from V , and integrating the result as before. A comparison of the results obtained by the two different methods is given in Table I, with values read from the curves of Pattee and Brown

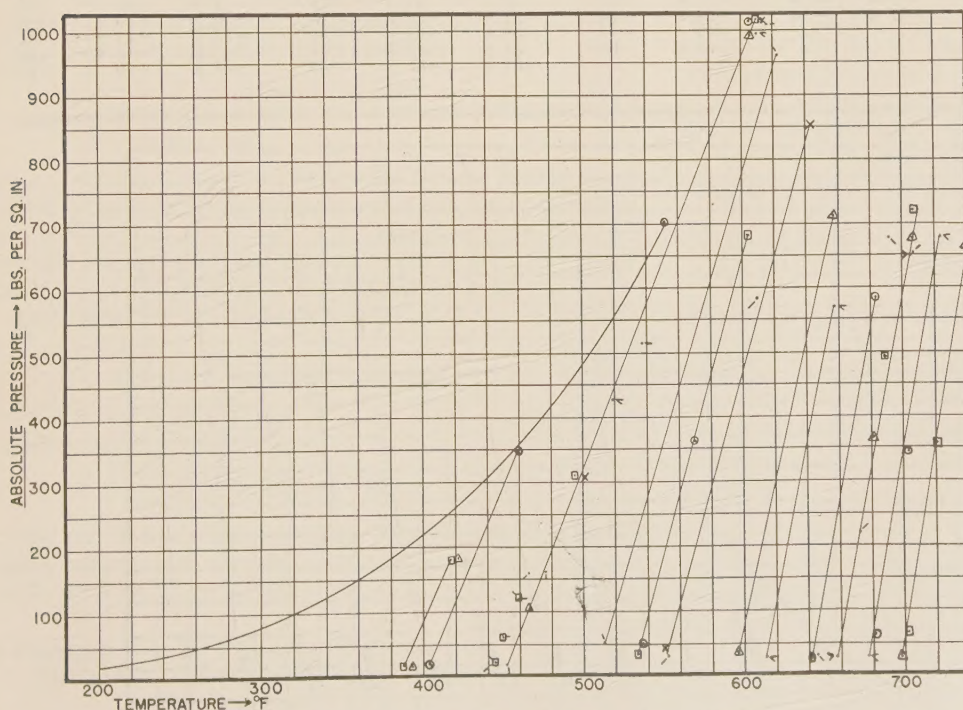


FIGURE 1. ORIGINAL DATA ON ISOENTHALPIC EXPANSION OF BENZENE

Each pair of symbols, along the same isenthalpic line, represent the initial and final pressures and temperatures observed. For example, Δ at 665 pounds per square inch and 741° F. indicates this as the initial pressure and temperature. The final state is also shown by Δ to be 30 pounds per square inch and 698° F. Along the same isenthalpic line, $\square$ indicates another experiment in which 357 pounds per square inch and 721° F. are the initial conditions and 67 pounds per square inch and 703° F. the final.

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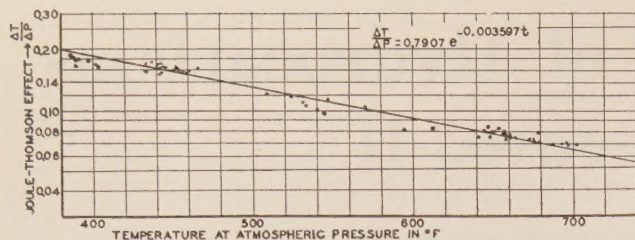


FIGURE 2. JOULE-THOMSON COEFFICIENT OF BENZENE

(5) based on direct determinations of the Joule-Thomson coefficient of pentane. The agreement between the experimental and computed results is good.

Enthalpy of Benzene Vapor

The apparatus and general procedure for determining the Joule-Thomson coefficient were similar to those already described (5). A radiant heater using radiation from electric resistance wires was substituted for the low-voltage resistance heater. The pump valve box was machined from a single steel bar and equipped with spool-shaped valves with leather seats. The pistons were packed with Johns Manville No. 323 with satisfactory results. The experimental results on benzene of c. p. grade are given in Table II.

When plotted as lines of constant enthalpy on a pressure-temperature diagram (Figure 1), the data of Table II give straight lines within the experimental limits. Therefore the slopes of these lines, as computed in Table II, enable the data

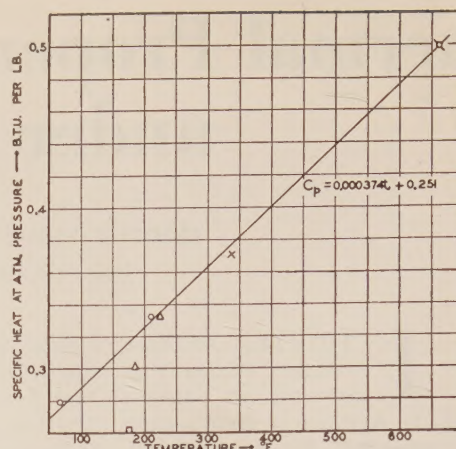


FIGURE 3. SPECIFIC HEAT OF BENZENE AT ATMOSPHERIC PRESSURE

○ Desjardin (1) △ Wiedmann (9) ϕ Thibout (7)
□ Leduc (4) × Regnault (6)

to be extrapolated to atmospheric pressure as indicated in the last column. The slopes are not identical for all temperatures but, when plotted on semi-log paper (Figure 2), were found to vary in the manner indicated by the following equation:

$$\frac{\Delta T}{\Delta P} = 0.7907 e^{-0.003597t} \quad (4)$$

where t = temp. at atm. pressure, ° F.

TABLE I. RELATIVE ENTHALPY OF *n*-PENTANE VAPOR

(In B. t. u. per pound, referred to atmospheric pressure at the indicated temperature)

Abs. Pressure, Lb./Sq. In.	-284° F.		-392° F.		-464° F.		-500° F.			536° F.		
	Analytical	Graphical	Graphical	Exptl.	Graphical	Exptl.	Analytical	Graphical	Exptl.	Analytical	Graphical	Exptl.
14.7	0	0	0	0	0	0	0	0	0	0	0	0
50	-3.8	-3	-2.8	-3	-2.8	-3	-2.6	-2	-2	-2.2	-2	-2
100	-7.7	-7.6	-5.7	-6	-5.5	-5	-5.0	-5.0	-5	-4.6	-5	-5
200	-17.8	-18.4	-12.4	-13	-11.4	-11	-10.1	-11.0	-11	-9.4	-11	-11
400			-32.4	-34	-24.0	-25	-21.6	-22.0	-23	-20.0	-20.7	-22
600					-41.7	-41	-35.8	-35.2	-38	-32.0	-31.8	-34
800					-66.6	-65 ^a	-51.6	-51.7	-52	-45.0	-45.4	-46
1000						..	-61.4	-67.8	-65 ^a	-56.3	-59	-57 ^a

^a Extrapolated.

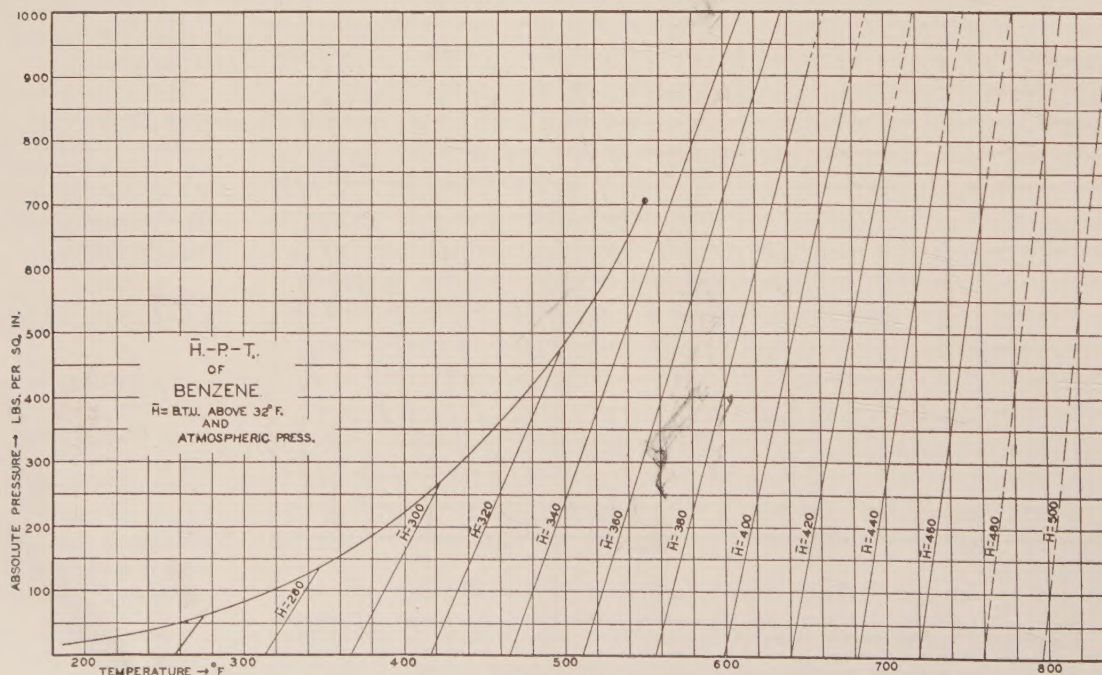


FIGURE 4. ENTHALPY-PRESSURE-TEMPERATURE RELATIONSHIPS OF BENZENE

TABLE II. RESULTS ON BENZENE

Run	Abs. Pressure, Lb./Sq. In.		Temperature, ° F.		ΔT , ° F.	ΔP , Lb./Sq. In.	$\frac{\Delta T}{\Delta P}$	t ° F. at 15 Lb. Pres- sure	Run	Abs. Pressure, Lb./Sq. In.		Temperature, ° F.		ΔT , ° F.	ΔP , Lb./Sq. In.	$\frac{\Delta T}{\Delta P}$	t ° F. at 15 Lb. Pres- sure
	High	Low	High	Low						High	Low	High	Low				
1	121	22	459	444	15	99	0.152	443	41	352	21	459	404	55	331	0.166	403
2	121	21	458	443	15	100	0.150	442	42	162	19	490	467	23	143	0.161	466
3	121	62	459	449	10	59	0.170	441	43	162	18	476	452	24	144	0.166	452
4	121	62	460	450	10	59	0.170	442	44	162	18	465	441	24	144	0.166	441
5	364	52	578	548	30	312	0.096	544	45	162	18	465	441	24	144	0.166	441
6	372	52	576	544	32	320	0.100	540	46	162	18	465	441	24	144	0.166	441
7	363	52	570	537	33	311	0.106	533	47	175	18	420	392	28	157	0.178	391
8	382	77	460	367	93	305	0.305	348	48	175	18	419	391	28	157	0.178	390
9	357	67	721	703	18	290	0.062	700	49	175	18	418	390	28	157	0.178	389
10	353	66	699	678	21	287	0.073	674	50	177	18	417	388	29	159	0.182	387
11	346	64	704	682	22	282	0.078	678	51	179	18	417	387	30	161	0.186	386
12	712	37	657	596	61	675	0.080	594	52	179	18	417	387	30	161	0.186	386
13	302	20	428	192	236	282	0.084	188	53	180	18	417	387	30	162	0.185	386
14	682	35	604	533	71	647	0.110	531	54	182	18	418	388	30	164	0.167	387
15	583	32	609	552	57	551	0.103	550	55	182	18	421	391	30	164	0.167	390
16	571	29	688	645	43	542	0.079	644	56	183	18	422	393	29	165	0.168	392
17	571	29	657	613	44	542	0.081	612	57	182	18	421	391	30	164	0.167	390
18	586	29	683	642	41	557	0.074	641	58	677	31	692	645	47	646	0.074	644
19	852	44	642	660	92	808	0.114	547	59	677	31	723	677	46	646	0.071	676
20	962	44	635	528	107	910	0.118	524	60	672	31	733	689	44	641	0.069	688
21	962	52	622	513	109	910	0.120	509	61	669	30	739	695	44	639	0.069	694
22	976	412	609	520	89	564	0.158	457	62	667	30	741	697	44	637	0.069	696
23	983	417	609	518	91	566	0.161	453	63	665	30	741	698	43	635	0.068	697
24	989	424	609	518	91	565	0.161	452	64	662	31	746	703	43	631	0.068	702
25	996	427	609	519	90	569	0.158	454	65	657	30	722	677	45	627	0.072	676
26	1010	517	614	537	77	493	0.156	459	66	655	30	724	680	44	625	0.071	679
27	1007	511	616	538	78	496	0.157	460	67	653	30	711	665	46	623	0.074	664
28	994	317	605	488	117	677	0.173	437	68	653	30	705	658	47	623	0.076	657
29	999	317	602	487	115	672	0.171	434	69	654	30	705	659	46	624	0.074	658
30	1008	312	606	487	119	686	0.173	434	70	655	30	709	662	47	625	0.075	661
31	1017	312	609	495	114	705	0.162	444	71	655	221	709	676	33	434	0.076	660
32	1017	312	611	497	114	705	0.162	446	72	655	221	709	676	33	434	0.076	660
33	1014	309	612	501	111	705	0.158	454	73	656	222	707	674	33	434	0.076	658
34	1012	112	607	464	143	900	0.159	449	74	656	221	707	673	34	435	0.078	657
35	1015	112	605	459	146	903	0.162	443	75	676	368	707	682	25	308	0.081	653
36	992	107	606	466	140	885	0.158	452	76	676	368	705	681	24	308	0.078	653
37	353	21	455	398	57	332	0.172	397	77	723	494	705	687	18	229	0.079	649
38	354	21	459	403	56	333	0.168	402	78	721	493	706	687	19	228	0.083	647
39	354	21	459	404	55	333	0.165	403	79	722	494	707	689	18	228	0.079	651
40	353	21	459	404	55	332	0.166	403									

The available specific heat data on benzene vapor at atmospheric pressure are in good agreement as indicated in Figure 3 and may be represented by the equation:

$$C_P = 0.000374t + 0.251 \quad (5)$$

where C_P = sp. heat, B. t. u./lb.
 t = temp., ° F.

The increase in enthalpy (ΔH) on heating benzene from liquid at 32° F. to vapor at 176°, under one atmosphere of pressure, is 232 B. t. u. per pound (2). Combining this value with the specific heat data for the benzene vapor gives the following equation as the enthalpy of superheated benzene vapor referred to liquid benzene at 32° F.,

$$\bar{H} = 232 + \int_{176}^t (0.000374t + 0.251) dt$$

which, when integrated, gives

$$\bar{H} = 0.000187t^2 + 0.251t + 182 \quad (6)$$

By use of Equations 4 and 6, lines of constant enthalpy may be drawn on a pressure-temperature diagram as shown in Figure 4.

Comparison of Effect of Pressure on Enthalpy of Benzene and Pentane Vapor

As a basis for comparison of the properties of different hydrocarbons, the reduced temperatures and pressures (found by dividing the absolute temperature or pressure by the

corresponding critical temperature or pressure) combined with the molecular quantity, have been found satisfactory. In Table III the calculated data for pentane, the experimental data for pentane (5) and for benzene have been compared on this basis, using 847° R. (387° F. + 460°) and 485 pounds per square inch absolute as the critical temperature and pressure for pentane, and 1011° R. and 702 pounds as the critical temperature and pressure for benzene.

The computed values of Table I were plotted to obtain values for the reduced pressures and temperatures as used in Table III, and the experimental values were read from the

TABLE III. COMPARISON OF EFFECT OF PRESSURE AT CONSTANT TEMPERATURE ON ENTHALPY OF PENTANE AND BENZENE VAPOR, ON BASIS OF REDUCED TEMPERATURES AND REDUCED PRESSURES

(In B. t. u. per pound mole per ° Rankine; values are for decrease in enthalpy per ° Rankine per pound mole, $-\Delta H/T$)

Reduced Pressure	Reduced Temperature = 0.9			Reduced Temperature = 1.0			Reduced Temperature = 1.1		
	Pentane Calcd.	Pentane Exptl.	Benzene	Pentane Calcd.	Pentane Exptl.	Benzene	Pentane Calcd.	Pentane Exptl.	Benzene
0.03	0	0	0	0	0	0	0	0	0
0.1	0.28	0.28	0.25	0.22	0.24	0.22	0.2	0.22	0.2
0.2	0.7	0.71	0.7	0.45	0.49	0.45	0.43	0.4	0.36
0.3	1.2	1.22	1.25	0.72	0.76	0.72	0.57	0.55	0.52
0.4	1.75	1.78	1.77	1.1	1.12	1.1	0.83	0.8	0.8
0.5	2.3	2.36	2.33	1.45	1.49	1.45	1.07	1.05	1.02
0.6				1.73	1.8	1.7	1.3	1.3	1.27
0.7				2.22	2.3	2.2	1.5	1.55	1.52
0.8					2.6	2.55	1.73	1.77	1.76
0.9					3.1	3.1	2.05	2.1	2.1
1.0					3.6	3.7	2.28	2.32	2.35
1.2							3.0	2.95	3.0
1.3						6.5			
1.4							3.8	3.85	3.9 ^a
1.6							4.43	4.5	

^a Extrapolated.

enthalpy-pressure-temperature charts for pentane (5) and benzene as in Figure 4. The values given in Table III represent the decrease in enthalpy per pound mole per ° Rankine (° F. + 460), or $-\Delta H/T$ referred to the enthalpy of the same vapor at the same temperature under a pressure of one atmosphere.

Literature Cited

- (1) Desjardin, *Ann. phys.*, **11**, 253 (1919).
- (2) Frock, Ginnings, and Holton, *Bur. Standards J. Research*, **6**, 893 (1931).
- (3) Gary, W. W., Rubin, L. C., and Ward, J. T., *IND. ENG. CHEM.*, **25**, 178 (1933).
- (4) Leduc, *Compt. rend.*, **152**, 1752 (1911).
- (5) Pattee, E. C., and Brown, G. G., *IND. ENG. CHEM.*, **26**, 511 (1934).
- (6) Regnault, *Inst. de France Mem. de l'Acad.*, **26**, 1 (1862).
- (7) Thibout, *Ann. Physik*, **35**, 347 (1911).
- (8) Weir, H. M., and Eaton, G. L., *IND. ENG. CHEM.*, **24**, 211 (1932).
- (9) Wiedmann, *Ann. Physik u. Chem.*, **2**, 195 (1877).
- (10) Young, Sidney, *Phil. Mag.*, **67**, 353 (1899).

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